

## A METHOD FOR THE DIRECT DETERMINATION OF ORGANIC NITROGEN BY THE KJELDAHL PROCESS.

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ONE of the most conspicuous recent advances made in sewage analysis in this country may be said to be the development of a direct process for the determination of the nitrogen as ammonia.<sup>1</sup> The greater simplicity of the technique, the greater economy of time effected by the elimination of distillation, and the relatively greater accuracy of the process are salient advantages of the direct method which surely cannot fail to be of moment in the routine work of sewage laboratories.

To be able to apply a direct process to the determination of the ammonia formed in the determination of total organic nitrogen by the Kjeldahl process seemed the next step toward greater simplicity and rapidity of execution. During a considerable portion of the work at Columbus a direct process was in daily use for the determination of the nitrogen as ammonia, and a more intimate knowledge was gained of local conditions as to the disturbing factor of turbidity, to which, as we all know, has been chiefly due the indifferent success attending earlier attempts at the direct nesslerization of the acid digestate of the Kjeldahl process. Under such circumstances it was thought that a direct method for determining nitrogen by the Kjeldahl process might be successfully developed.

Working along lines by which a direct process for the determination of the nitrogen as free ammonia was successful under such unusually hard water conditions as prevailed at Columbus, a method was finally obtained by which the disturbing turbidity was completely eliminated. It is our purpose to discuss the several factors which have to do with the turbidity occurring in nesslerized tubes, and further to describe a direct method for determination of nitrogen by the Kjeldahl process, found applicable under Columbus condi-

tions, together with certain suggestions whereby it appears that the direct method may be made of quite extended applicability.

#### METHODS PREVIOUSLY PROPOSED.

A review of the literature upon the question of the direct nesslerization of the acid digestate of the Kjeldahl process indicates that the matter has received but little attention. So far as we are aware, the method described by Rideal,<sup>2</sup> a similar one used to some extent by McGowan,<sup>3</sup> and the modifications suggested by Phelps,<sup>1</sup> are the only instances on record in which the feasibility has been suggested of the elimination of distillation in Kjeldahl nitrogen determinations. Rideal states that the direct determination of the organic nitrogen has been practiced to some extent in England. The method as given by him is as follows:

*"Kjeldahl.*—10 c.c. of a sewage, or say, 100 c.c. of an effluent plus 4 c.c. of pure sulphuric acid, are heated in a pear-shaped hard glass flask in a slanting position until the liquid becomes colorless. When about 2 or 3 c.c. remain, the flask is cooled and is washed out with small quantities of ammonia-free water into a 100 c.c. measure, until the volume of the liquid reaches about 40 c.c. An excess, i. e., about 25 c.c., of soda solution (25 per cent) free from ammonia is now added, when a flocculent precipitate is thrown down. After cooling, the liquid is made up to 100 c.c., transferred to a clean and dry stoppered bottle, and shaken at intervals until the flocculi—which at first float entangled with air bubbles—subside. A suitable fraction of the clear liquid is then pipetted into a Nessler glass, diluted to 50 c.c., and nesslerized. *This gives the total unoxidized nitrogen in terms of ammonia.*"

This method was used by McGowan,<sup>3</sup> modified only by the occasional addition of potassium oxalate solution to the alkaline digestate to precipitate the calcium, and by the proviso that the solution should be "rendered *just* alkaline with purified potash." The method is criticised by McGowan on the ground that turbidity is oftentimes noted, even when the calcium has been removed by the addition of oxalate solution, and that considerable entrainment of ammonia results from the precipitate formed upon the neutralization of the digestate. His chief objection to the process seems to be that where considerable amounts of nitrified nitrogen are present, all of the unoxidized nitrogen is not recovered, since, during the last stages of the digestion, a portion of this nitrogen is oxidized by the nitric acid present and is probably lost in the form of lower oxides of nitrogen. For this reason the English practice in regard to the Kjeldahl method for effluents includes a reduction of all nitrified

nitrogen by the use of zinc and sulphuric acid. This portion of the procedure is stated by English workers to require five days for its completion; for otherwise, as their experience indicates, an appreciable loss of nitrogen will ensue. The discussion is concluded with the statement that although the direct method—with no reduction of nitrate—has been found at times to yield very satisfactory results in the analysis of very pure effluents, and frequently in others containing as high as 5.0 parts per million nitrogen as nitrate, yet, for general work upon sewage and sewage effluents, experience seems to be against the method, since no preliminary reduction of nitrate is included in the technique.

In this country, Phelps has outlined a method which he used with somewhat indifferent success, owing, as he states, to certain factors associated with the turbidity of the nesslerized tubes, which as yet are not clearly understood. The method employed by him consisted in making up the digestate to 250 c.c., removing 2 c.c., neutralizing, making up to 50 c.c., and directly nesslerizing.

In the nitrogen work at the Columbus Sewage Testing Station a study was made of the feasibility of adopting a direct method for the determination of the ammonia formed in the Kjeldahl process, along the lines suggested by the studies of previous workers to which we have just referred. With some modifications, the methods described by Rideal and McGowan have been found to yield satisfactory results when applied to the sewage and effluents under study at Columbus. Those changes were the results of an extended inquiry into the causes of the disturbing turbidity which, as we all know, has been the chief drawback to the applicability of the direct process. The results of these studies have been incorporated in the technique of the method as given below, and it is felt that the method, when modified along lines to be suggested in order to meet different conditions, gives promise of a fairly wide field of applicability in the analysis of sewage and sewage effluents.

#### FACTORS ASSOCIATED WITH THE TURBIDITY PRODUCED BY DIRECT NESSLERIZATION.

The cause of the disturbing turbidity which appears upon the addition of Nessler's reagent to solutions containing other salts as well as ammonium salts, has been chiefly attributed to the presence

therein of calcium salts. Considering for the moment such conditions as would obtain in direct nesslerization, without treatment with caustic soda, of an aliquot portion of a hard sewage containing the bicarbonates of calcium and of magnesium, respectively, and, in addition, both these metals as incrustants, it follows from water-softening experience that the addition of the caustic Nessler's reagent will entail a precipitation of a portion of the calcium as carbonate, and the whole of the magnesium as hydrate, whereby cloudiness would result. Such seems to be one of the explanations of the failure of attempts to obtain clear tubes when small amounts of a hard sewage, or sewage containing but moderate amounts of the alkaline earth metals, diluted to the usual 50 c.c., have been directly nesslerized, or when, as in Phelps's method, a small portion of the acid digestate is neutralized and nesslerized without preparatory treatment for the removal of the magnesium, and in certain cases of calcium as well.

The method as advised by the Committee on Standard Methods for the determination of the nitrogen as free ammonia by direct nesslerization, appears to admit of adoption under a wide range of conditions with respect to the mineral constituents of the sewage, for the reason that the preparatory treatment of the sample with caustic alkali effects a complete softening of a hard sewage, removing to a sufficient degree the carbonate of calcium, all of the magnesium, and a variable proportion of calcium sulphate, depending upon the relative amount of half-bound carbonic acid present. The development of a successful method for the direct nesslerization of ammonia has clearly resulted from the use of a preparatory treatment which softens the sewage materially, thereby removing before nesslerization those substances which, by precipitating in the nesslerized tubes, caused the turbidity so often observed.

Coming now to the premises of the paper, the thought arises as to wherein the conditions differ from those obtaining in the successful direct determination in hard sewages of the nitrogen as free ammonia. As is well known, under certain conditions the metals of the alkaline earth group, when present in a nesslerized tube, obscure by precipitation the clear yellow of the mercurio-ammonium compound, and thus the question of the turbidity of the neutralized and nesslerized

lerized acid digestate would appear to revert to the interference of calcium and magnesium salts, and, further, possibly to the presence of sodium sulphate from the neutralization of the sulphuric acid.

A little thought will suggest that, irrespective of the nature of the acid radicals to which the calcium and the magnesium are united in the sewage, they are in combination, after digestion, with sulphuric acid as sulphates. The neutralization of the acid digestate with a sufficient excess of alkali removes the magnesium as in the direct ammonia procedure, so that, so far as these metals are concerned, the question of turbidity would appear to refer to the presence, of calcium as sulphate, which is not removed upon the neutralization of the acid digestate with carbonate-free caustic soda. We have found by experiment that calcium as sulphate may be present in a nesslerized tube without causing precipitation, to the extent of 50 parts per million of calcium (Ca). Above this amount, up to the limit of the solubility at ordinary temperatures of calcium as sulphate of 100 parts per million of calcium (Ca), turbidity will be noted. Under ordinary conditions, calcium in this form is probably not a factor; but to avoid possible complications, under conditions to be referred to later, it would seem advisable to add to the digestate a certain amount of carbonate of soda, for the removal of the calcium, imitating conditions obtaining in most cases in the direct nesslerization of the nitrogen as ammonia. To study the effect of the presence of sodium salts, a blank digestate was neutralized and carried through the usual procedure, as given below, and in no case did any turbidity appear to be traceable to this source.

Taking into account each of the factors just discussed, efforts to obtain clear tubes continued to be indifferently successful, until finally it developed that the character of the caustic soda used for neutralization was related to the intensity of the turbidity of the nesslerized tubes. The so-called C. P. stick caustic soda is far from pure, as is well known, and it was found that the usual treatment for the removal of ammonia was not sufficient to prevent a precipitation in nesslerized tubes containing free alkali. To remove ferrous iron, organic matter, or any chance reducing agent to any of which the turbidity would appear to be due, caustic soda was prepared, by oxidation with either sodium peroxide or permanganate, as

described below. With caustic solutions prepared in this manner, fairly satisfactory results were obtained.

Up to this time the method described by Palmer<sup>5</sup> had been used, wherein permanganate is added to the digestion when it is judged to be complete. In reviewing possible causes of the disturbing turbidity, the thought suggested itself that the presence of manganous sulphate, even in small amounts, would tend to produce turbidity, because of the ease with which the salt is oxidized and precipitated in alkaline solutions. Experiments with solutions containing manganous sulphate (formed when permanganate is used) showed conclusively, as was expected, that turbid tubes would result upon nesslerization. As the use of permanganate is of uncertain value as an aid in the oxidation by sulphuric acid of the substances found in ordinary sewage, following the practice of Rideal,<sup>2</sup> the addition of permanganate at the end of the digestion was omitted from the procedure as finally adopted, on the ground that a certain amount of manganous sulphate might escape oxidation during the preparation of the digestate for nesslerization, whereby turbid tubes would result.

By the use of a caustic soda solution free from oxidizable organic matter, clear tubes were finally obtained, provided that a sufficient excess of caustic was added to precipitate completely the magnesium, and provided that sodium carbonate was added to remove the calcium.

Considerable literature is available upon the use of Nessler's reagent, and from the work of Nessler,<sup>6</sup> Miller,<sup>7</sup> Chapman,<sup>8</sup> Frankland and Armstrong,<sup>9</sup> Trommsdorff,<sup>10</sup> and Fleck,<sup>11</sup> it appears that both free alkali and the presence of magnesium, or the formation in the tubes of any other precipitate whatsoever, affects the color produced by the reagent. The alkali tends to give abnormally high readings, and the co-precipitation of any other substance, together with the mercury ammonium iodide, completely coagulates the colloidal color produced by Nessler's reagent in pure solutions of ammonium salts. In connection with the question of the direct nesslerization under hard water conditions at least, it is a significant fact that the use of a magnesium salt forms the basis of Fleck's titration method<sup>11</sup> for the determination of ammonia by Nessler's reagent, wherein the mercury ammonium iodide, completely precipitated by magnesium,

is dissolved in sodium thiosulphate and titrated with an ammoniacal solution of silver sulphide.

It is evident that an excess of alkali will remove the magnesium. To determine the limit to which the excess could be carried with safety, different amounts of differently prepared caustic soda solutions, ranging by roths to one gram, respectively, were added to Nessler tubes containing 3 c.c. of ammonia standard. The tubes were filled to the mark with ammonia-free water, and were then nesslerized. The colors were read after 15 minutes. It appears from the results in the table below that 0.2 gram of pure caustic (NaOH) may be present in a nesslerized tube without producing turbidity or causing the color to be abnormal. Beyond this amount, turbidity, and finally complete precipitation, will result, as will also be the case when impure caustic is used without an oxidizing treatment.

Above 0.5 gram a heavy precipitate was observed in all cases.

TABLE 1.

EFFECT OF THE PRESENCE OF CAUSTIC SODA UPON THE COLOR PRODUCED BY NESSLER REAGENT.

CAUSTIC SODA (NaOH)  (Gram)	TREATMENT RECEIVED BY CAUSTIC*							
	NONE				SODIUM PEROXIDE		PERMANGANATE	
	FUSED STICK		BY ALCOHOL					
	Reading	Turbidity	Reading	Turbidity	Reading	Turbidity	Reading	Turbidity
	0.0.....	3.0	o	3.0	o	3.0	o	3.0
0.1.....	...	str.	3.0	o	3.0	o	3.0	o
0.2.....	...	"	3.0	o	3.0	o	3.0	o
0.3.....	...	"	3.1	o	3.1	o	3.2	o
0.4.....	...	"	3.5	sl.	3.3	v. sl.	3.5	v. sl.
0.5.....	...	"	3.8	str.	3.5	str.	3.6	str.

\*Fused white sticks.

By including in the final details of the method an excess of alkali corresponding to 2 c.c. of 25 per cent caustic soda, or 5.0 gram of the alkali giving in the nesslerized tubes only one-tenth of this amount and adding 0.2 gram of sodium carbonate to the alkali digestate, clear tubes were finally obtained. The method employed takes into account the following factors, which our experience indicates as the controlling causes of turbid tubes in direct nesslerization work:

a) Insufficient preparatory treatment of the sample, whereby there results a precipitation of calcium carbonate or of magnesium hydrate,

and, in general, the formation by the alkali of the Nessler's reagent of any other precipitate whatsoever save the normal colloidal mercury ammonium iodide.

b) The use of caustic soda containing organic matter.

c) The presence of a manganous salt from the use of permanganate in the digestion.

d) The presence in the nesslerized tubes of calcium as sulphate in hard sewages above 50 parts per million, and, further, the neglect to mix thoroughly the solution before nesslerizing, even in cases where the calcium in a tube containing a homogeneous solution would be below the limiting value of 50 parts per million.

#### DETAILS OF THE COLUMBUS METHOD FOR THE DIRECT DETERMINATION OF NITROGEN BY THE KJELDAHL PROCESS.

Although subject to considerable modifications from time to time, to correspond to developments in the study of the turbidity question, the Columbus method for the direct determination of nitrogen by the Kjeldahl process finally assumed the following definite shape:

*Reagents.*—Aside from the preparation of the caustic, the use of a sodium carbonate solution, and the omission of permanganate, the reagents do not differ from those used in the standard Kjeldahl process.<sup>5</sup> Two brands of caustic soda were used, one the ordinary fused white sticks, the other caustic soda from alcohol. Both require a certain amount of oxidation to remove all organic matter. This has been effected either by the addition of about 2 per cent of sodium peroxide to the caustic solution prepared from caustic by alcohol, or, in case the ordinary fused white stick caustic, which is somewhat cheaper than that from alcohol, is used, by the use of potassium permanganate as follows:

Caustic soda solution: Dissolve in a liter of redistilled water 250 grams of fused white stick caustic soda. Heat to boiling and add a strong solution of potassium permanganate, drop by drop, until a pale-green color persists; continue to boil to expel ammonia and to cause a precipitation of the manganic oxide.

If the conditions are right, the caustic solution will assume a coffee-brown color, due to the suspended manganic oxide. In cases where the caustic is desired for immediate use, the solution, when cooled sufficiently, is filtered through asbestos by the aid of a filter pump; the resulting filtrate should be perfectly colorless, and free from suspended matter. Where time permits, the turbid solution may be allowed to stand until the precipitate shall have subsided.

Carbonate of soda solution: Dissolve 100 grams of C. P. anhydrous salt in one liter of ammonia-free distilled water.

*Method.*—Measure out such an amount of the sample as will contain between 0.00050 and 0.00100 gram of nitrogen; that is, an amount which will be equivalent to from 50 to 100 c.c. of the nitrogen ammonia standard; and digest with 5 c.c. of sulphuric acid, until the liquid is colorless or, in the presence of iron, shows a pale-



yellow color which becomes white when the solution has cooled. Rinse the acid digestate into a 50 c.c. flask, allow to cool to room temperature, fill to the mark, and mix thoroughly by inverting the flask at least four times. Place 25 c.c. of this solution in a 100 c.c. flask, preferably glass-stoppered, and add an amount of caustic soda solution not quite sufficient to neutralize the acid completely. Immerse the flask in ice-water to effect a rapid cooling. When cool, add more caustic soda solution from a pipette, drop by drop, until a flocculent precipitate is plainly visible. Add then 2 c.c. of the sodium carbonate solution. Make up to the 100 c.c. mark, stopper the flask, and mix thoroughly. Pour the solution into a clean four-ounce white glass bottle, preferably tall, and allow to stand at least six hours, shaking slightly at intervals in case the flocculi do not tend to settle readily. Pipette 10 c.c. of the completely clear, colorless supernatant solution into a 50 c.c. Nessler tube, make up to the mark with ammonia-free water, and mix thoroughly by inverting the tube. Nesslerize as usual and read after 15 minutes. The nesslerized tubes should show no turbidity. As in all Kjeldahl methods, a reagent blank must be subtracted from each determination. The results are computed as follows:

$$\frac{(N \times 20) - \text{Blank}}{S} \times 1,000,000 \times .0001$$

Where  $N$  = c.c. standard reading

$S$  = c.c. sample digested.

The results are in terms of the *total unoxidized nitrogen* in the sample. The *organic nitrogen* is determined by subtracting from these results the amount of ammoniacal nitrogen determined by a direct process.<sup>12</sup>

#### DISCUSSION OF CERTAIN IMPORTANT FEATURES OF THE METHOD.

There are several points relative to the method, which our experience has shown to be very essential to the attainment of satisfactory results.

**Turbidity.**—To avoid cloudy tubes a period of subsidence of at least six hours is necessary both to insure a clear supernatant solution and also to effect a complete precipitation of the slowly forming calcium carbonate. Further, sufficient carbonate of soda must be present to precipitate the calcium, and a sufficient excess of purified caustic soda solution is necessary for the complete removal of magnesium. An excess of 0.05 gram caustic soda (NaOH) was found to be sufficient. Since, as pointed out above, 0.2 gram of free caustic alkali does not appear to interfere with Nessler's reagent, 0.05 gram of alkali, the amount in each tube, may be safely used, thus insuring a complete precipitation of magnesium.

**Neutralization.**—The neutralization has been completed in two stages, cooling the solution before alkalinity obtains to guard against any possible loss of ammonia. Ice-water has been found convenient as a cooling agent.

*Apparatus and technique.*—In the technique of the method, ordinary graduated volumetric flasks have been used for making the necessary measurements, and for mixing the several solutions. For general practice it would certainly be advantageous to use glass-stoppered 50 and 100 c.c. flasks, respectively, in order that mixing may be carried on without contamination and without injury to the hands.

The containers in which the neutralized digestates are allowed to settle should preferably be tall, in order to facilitate the subsequent pipetting of the supernatant solution. During subsidence, the bottles should be protected from dust and carbonic acid, and to this end it is suggested that glass-stoppered bottles of about 120 c.c. capacity, contained in suitable racks, could be advantageously used to protect the determination prior to the completion of the process.

#### RELATIVE RESULTS FROM THE DIRECT AND DISTILLATION PROCESS, RESPECTIVELY.

In the work at Columbus, before substituting the direct method for the distillation process in current use, a sufficient number of comparative analyses were made to insure that the results should be strictly comparable to those of the older method. At the same time, it was thought that the simpler technique of the direct method and the elimination of all factors of error associated with the distillation might be the means of giving somewhat higher results. Representative results are shown in the table below, from which it appears that the results by the direct process are substantially the same as those obtained by the distillation of the neutralized digestates. The differences observed in the results by the two methods are so slight as to be outweighed, from a practical standpoint, by the very great saving of time effected by the use of the direct process.

#### ENTRAINMENT OF AMMONIA.

One of the objections to the direct process raised by McGowan<sup>3</sup> refers to the possible loss of ammonia through absorption by the precipitate formed when the acid solution of the digestate is neutralized, or when, as in the direct determination of the nitrogen,<sup>4</sup> as free ammonia a more or less heavy precipitate forms upon the addition of alkali. McGowan made experiments to illustrate this by nesslerizing a

TABLE 2.  
REPRESENTATIVE ORGANIC NITROGEN RESULTS BY KJELDAHL—COMPARISON OF THE DIRECT AND  
DISTILLED METHODS.

Parts per Million—Nitrogen.

SOURCE OF SAMPLE	ORGANIC	
	Direct	Distilled
Crude sewage.....	10.1 4.5 9.0 10.3	9.7 4.5 8.6 9.9
Settled sewage.....	4.9 10.7 5.1 13.9	4.7 10.3 5.1 14.0
Septic sewage.....	5.4 4.7 5.4 7.0	5.4 5.2 5.1 7.4
Coarse-grain filter effluent.....	4.7 3.9 2.2 1.8	5.2 3.9 2.2 1.8
Ditto settled.....	3.5 1.8 2.1 3.6	3.7 1.9 2.2 3.0
Sand filter effluents.....	0.67 0.37 0.53 0.65	0.66 0.44 0.50 0.54

portion of the clear liquid in the direct Kjeldahl process, then shaking up the precipitate in the remaining liquid, subjecting the turbid solution to distillation, and determining the amount of ammonia in an aliquot portion of the distillate. He shows that an appreciable entrainment of ammonia results, but adds that a stricter comparison would have been effected had both the clear and the turbid liquid been subjected to distillation. Phelps,<sup>1</sup> in a recent paper upon the determination of ammonia in sewage, alludes to the entrainment factor, which he substantially eliminates by diluting the sample in which it is desired to determine the nitrogen as free ammonia before the addition of alkali.

*Entrainment experiments.*—To study this point under Columbus conditions, a portion of the clear supernatant solutions from the nitrogen as free ammonia and from the total nitrogen determinations, respectively, were nesslerized as usual, following which 40 c.c. of the alkaline solutions, containing probably all of the precipitate, were respectively dissolved in small amounts of sulphuric acid. The solutions were then diluted to 100 c.c., and the calcium and magnesium salts again precipitated by the addition of caustic soda. Aliquot portions of the clear supernatant solutions, corresponding in amounts of ammonia to those in the original determinations, were then diluted to 50 c.c., and the ammonia determined as usual. If the entrainment factor were one of appreciable moment, it was thought that the ammonia reading in the tubes from the

second precipitation would be correspondingly higher than those obtained in the original determination, since the second digestion contained practically all the precipitate formed in the initial precipitation. Since practically the same readings were obtained in both cases and in both of the direct methods, the indications are that the entrainment factor is not of sufficient moment, from a practical standpoint, to render the results of direct processes unreliable. Experimental results upon the absorption factor are shown in the following table:

TABLE 3.  
EFFECT OF ENTRAINMENT UPON RESULTS OF DIRECT NESSLERIZATION.  
Nitrogen as Free Ammonia—Direct Kjeldahl.

NUMBER	STANDARD READING			
	A	B	A	B
1.....	4.0	3.9	2.4	2.4
2.....	3.5	3.5	2.9	2.9
3.....	3.5	3.5	2.2	2.2
4.....	3.1	3.1	2.9	2.7

NOTE.—A=Supernatant from first precipitation; B=ditto from second precipitation.

#### DISCUSSION OF THE GENERAL APPLICABILITY OF THE DIRECT PROCESS IN SEWAGE WORK.

In considering the method for the direct determination of the total unoxidized nitrogen by the Kjeldahl process, which has been found applicable for Columbus conditions, where unusually large amounts of calcium and magnesium are encountered, with respect to its applicability for sewages common to New England and to other places where soft water conditions are as a rule more in evidence, Columbus experience leads us to believe that the method can be successfully used. Since a digestate must be freed from the alkaline earth metals before a direct treatment with Nessler's reagent is attempted, it would seem, in the absence of the complicating salts of hard sewages, that no difficulty would be experienced in obtaining clear tubes.

In this connection it may be stated that the direct process has been applied in the Columbus work to the determination of total nitrogen in bacterial culture media work, in connection with studies of denitrification such as have recently been brought forward at the Lawrence Experiment Station.<sup>13</sup> Excellent results were obtained by the direct nesslerization of aliquot portions of neutralized digestates, in which the Gunning modification<sup>14</sup> of the Kjeldahl process was employed.

For soft-water sewages the method appears to be applicable. Even for harder sewages than a maximum of about 600 parts per million as calcium carbonate, encountered under Columbus conditions, it is thought that the calcium in solution as sulphate would be reduced below 50 parts per million in the nesslerized tubes by the addition of sodium carbonate, and in view of the fact that calcium as sulphate is not soluble over 100 parts per million<sup>15</sup> in pure water and probably much less so in solutions of sodium sulphate. In the case of a very hard sewage, or where a moderately hard sewage low in nitrogen is examined, as we have often noted, considerable calcium sulphate separates out when the digestate is diluted to a volume of 50 c.c. In all cases, therefore, the added sodium carbonate should be sufficient to remove all of the interfering calcium, even when present to the limit of its solubility.

#### APPLICATION TO WATER ANALYSIS.

Outside of the field of sewage analysis is the question of the feasibility of using a direct process in the sanitary analysis of water, in those cases where the total organic nitrogen is determined by the Kjeldahl method. No literature upon this matter has come to our attention.

By modifying the technique to include the neutralization of the entire digestate, with the addition of the usual excess of caustic soda, by adding a suitable amount of sodium carbonate, and by nesslerizing up to 50 c.c. of the alkaline digestate, it appears highly probable that a direct process might be used in water work. We would be inclined to place the limit of total nitrogen obtainable with the direct process at 0.1 part per million.

For such small amounts of total unoxidized nitrogen, complete softening is absolutely essential to the success of direct nesslerization. Moreover, since the direct process for the determination of the nitrogen as free ammonia cannot be applied to the determination of such small amounts as usually accompany low total unoxidized nitrogen values, the advantages of a direct process are not so apparent, especially since distillation processes give small amounts of ammonia with such relatively greater accuracy than can be obtained by a direct process, in which errors of multiplication are always an accompanying feature. It is felt, however, that the direct process may have a certain field of

usefulness for fairly polluted waters, and it is hoped that the suggestions made herein may be of some value to other workers, to whom the opportunity may be given for studying the further development of the direct process along lines which we have not been able to pursue under the hardness conditions obtaining at Columbus.

In conclusion, we desire to express our thanks to Mr. Julian Griggs, chief engineer of the Board of Public Service, Columbus, Ohio, by whose permission we have been enabled to present the results of these analytical studies before the publication of the report of the Testing Station. We wish also to express our appreciation of the valued criticisms of Mr. George W. Fuller, consulting engineer, and the valuable suggestions of Mr. George A. Johnson, engineer in charge of the Testing Station.

#### BIBLIOGRAPHY.

1. a) FARENSTEINER, BUTTENBURG, AND KORN. *Leitfaden d. chem. Untersuch. von Abwässer*, Hamburg.
- b) PHELPS. "Determination of Ammonia in Sewage." *Jour. Infect. Dis.*, 1904 1, p. 327. *Contributions Sew. Exp. Sta. Mass. Inst. Tech.*, 1905, 1, p. 87.
2. RIDEAL. *Sewage*. 2d ed., 1901., p. 39.
3. MCGOWAN. *Fourth Report Royal Com. on Sew. Disp.*, 4, Pt. 5, p. 35.
4. *Report of Committee on Standard Methods*, Am. Pub. Health Assoc. Rep., 1905, 31, p. 35; also *Jour. Infec. Dis.*, 1905, Supplm. No. 1, p. 1.
5. PALMER. *Report of Streams Examination*, Sanit. Dist., Chicago, Ill., 1902, p. 60.
6. NESSLER. *Tiemann-Gärtner's Handbuch*, 1905, p. 114.
7. MILLER. *Ztschr. j. Anal. Chem.*, 1865, 4, p. 459.
8. CHAPMAN. *Ibid.*, 1868, 7, p. 478.
9. FRANKLAND AND ARMSTRONG. *Jour. Chem. Soc.*, 1868 (2), 22, p. 77.
10. TROMMSDORFF. *Ztschr. j. Anal. Chem.*, 8, 1869, p. 357.
11. FLECK. *Jour. j. prakt. Chem.*, 1872 (2), 5, p. 263.
12. Forthcoming *Report*, Sewage Testing Station, Columbus, Ohio.
13. CLARK AND GAGE. *Eng. News*, 1905, 53, p. 27.
14. WILEY. *U. S. Dept. Agric. Bulletin 46*, rev. ed., p. 17.
15. H. DE LA COUX. *L'eau dans l'industrie*, Paris, 1900, p. 53.